GOLF BALL COMPRISING HIGHER COEFFICIENT OF RESTITUTION CORE AND METHOD OF MAKING SAME

FIELD OF THE INVENTION

The present invention is directed to golf balls including improved polybutadiene compositions for use in producing molded golf ball cores. Additionally, the present invention is directed to golf balls including a molded core formed from a polybutadiene rubber exhibiting a solution viscosity value that is correlated to the coefficient of restitution value of the molded core. The present invention is also directed to cores and/or golf balls produced by utilizing such a correlation, and/or to methods of making the same.

BACKGROUND OF THE INVENTION

The composition of a golf ball core affects the properties of a golf ball in many ways. Particularly, the golf ball core composition affects the playability and durability properties of a golf ball. Currently, golf ball cores are typically formed from a synthetic polybutadiene rubber composition. The polybutadiene rubber composition provides resilience to the golf ball, while also providing many desirable properties to both the core and golf ball, including weight, compression, coefficient of restitution (C.O.R.), etc.

The C.O.R. is a particularly important golf ball property. The resilience or C.O.R. of a golf ball is the constant "e," which is the ratio of the relative velocity of an elastic sphere after direct impact to that before impact. In other words, the C.O.R. is the ratio of the outgoing velocity to the incoming velocity. As a result, the C.O.R. ("e") can vary from 0 to 1, with 1 being equivalent to a perfectly or completely elastic collision and 0 being equivalent to a perfectly or completely inelastic collision.

The C.O.R. in solid core golf balls is a function of the composition of the molded core and cover. The molded core and/or cover may be comprised of one or more layers such as in multi-layered balls. In balls containing a wound core (i.e., balls comprising a liquid or solid center, elastic windings, and a cover), the coefficient of restitution is a function of not only the composition of the center and cover, but also the composition and tension of the elastomeric windings. As

in the solid core balls, the center and cover of a wound core ball may also consist of one or more layers.

C.O.R., along with additional factors such as club head speed, club head mass, ball weight, ball size and density, spin rate, angle of trajectory and surface configuration (i.e., dimple pattern and area of dimple coverage) as well as environmental conditions (e.g. temperature, moisture, atmospheric pressure, wind, etc.) generally determine the distance a ball will travel when hit. Along this line, the distance a golf ball will travel under controlled environmental conditions is a function of the speed and mass of the club and size, density and resilience (C.O.R.) of the ball and other factors. The initial velocity of the club, the mass of the club and the angle of the ball's departure are essentially provided by the golfer upon striking. Since club head, club head mass, the angle of trajectory and environmental conditions are not determinants controllable by golf ball producers, and the ball size and weight are set by the United States Golf Association (U.S.G.A.), these are not factors of concern among golf ball manufacturers. The factors or determinants of interest with respect to improved distance are generally the coefficient of restitution (C.O.R.) and the surface configuration (dimple pattern, ratio of land area to dimple area, etc.) of the golf ball.

There is no U.S.G.A. limit on the C.O.R. of a golf ball, but the initial velocity of the golf ball must not exceed 255 feet per second. As a result, the industry goal for initial velocity is 255 feet per second, and the industry strives to maximize the C.O.R. without violating this limit. Having the longest ball--compatible with the U.S.G.A. requirements--has been and also remains another longstanding objective of golf ball manufacturers. In this respect, prior balata and polymeric covered balls, and certainly those intended for U.S.G.A. regulation play, have shared one thing in common. They have all relied on their preformed cores as the primary vehicle for transferring energy from the golf club to the ball when the ball is struck by the club. For years, the principal thrust of golf ball research and development has been directed to making improved preformed cores for enhancing distance performance. In other words, conventional wisdom among golf ball manufacturers has been that enhanced

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distance performance is primarily achievable through cores formed from improved core compositions.

The C.O.R. must be carefully controlled in all commercial golf balls if the ball is to be within the specifications regulated by the U.S.G.A. As mentioned to some degree above, the U.S.G.A. standards indicate that a "regulation" ball cannot have an initial velocity exceeding 255 feet per second in an atmosphere of 75 °F when tested on a U.S.G.A. machine. Since the C.O.R. of a ball is related to the ball's initial velocity, it is highly desirable to produce a ball having sufficiently high C.O.R. to closely approach the U.S.G.A. limit on initial velocity, while having an ample degree of softness (i.e., hardness) to produce enhanced playability (i.e., spin, etc.).

Present core compositions in golf balls are typically formed from polybutadiene rubbers under the TAKTENE® (Bayer AG) or CARIFLEX® (Shell Chemical) trademark designations, including under the particular TAKTENE® 220 and CARIFLEX® BR-1220 polybutadiene rubber designations. TAKTENE® or CARIFLEX® polybutadiene compositions and the core compositions formed from those polybutadiene rubbers exhibit well-known properties, including P.G.A. and Riehle compression, solution viscosity and C.O.R. properties. The properties of TAKTENE® or CARIFLEX® polybutadiene rubbers and the core compositions formed from these polybutadiene rubbers, however, are within a particular well known range, and thus, the properties are limited if one desired a core composition having improved properties outside of these known property ranges.

Due to the continuous importance of improving the properties of a golf ball, particularly the C.O.R. of a golf ball, it would be beneficial to form a golf ball core composition from a polybutadiene rubber that exhibits improved properties, particularly improved C.O.R., over known golf ball core compositions. It would also be beneficial to be able to exhibit a particular C.O.R. for a core composition based upon a particular property within the polybutadiene rubber.

SUMMARY OF THE INVENTION

The present invention relates to golf ball cores having a particular C.O.R. value formed from a polybutadiene rubber having a particular solution

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viscosity and methods for making such cores. The polybutadiene rubber that forms the composition exhibits a particular solution viscosity value that is related to the C.O.R. value of the resulting molded core, so that the higher the solution viscosity value of the polybutadiene rubber, the higher the C.O.R. value of the core. This is while the solid Mooney viscosity of the polybutadiene rubber remains relatively constant.

The present invention further relates to golf balls including a core formed from a composition having a polybutadiene rubber exhibiting a solution viscosity that is directly related to the C.O.R. value of the finished molded core, and methods for making such a golf ball. As previously stated, it has been found that at a constant Mooney viscosity, the higher the solution viscosity of the polybutadiene rubber, the higher the C.O.R. value of the resulting molded core. Therefore, the present invention also relates to higher C.O.R. cores formed from core compositions having higher solution viscosities than other known core formulations, at similar solid Mooney viscosities and methods for forming and/or producing such cores.

In an additional aspect, the present invention is directed to golf balls comprising a core formed from a polybutadiene rubber. The polybutadiene rubber exhibits a solution viscosity of greater than 70 mPa•s, preferably greater than 80 mPa•s, and more preferably greater than 90 mPa•s, at a constant solid Mooney viscosity of about 38 to about 52, preferably about 45 ± 5. The golf ball also includes one or more core and/or cover layers generally surrounding the core, either alone or in combination with other layers of materials.

In a further aspect, the present invention is directed to golf balls comprising a core formed from a core composition including a polybutadiene rubber exhibiting a solution viscosity of about 90 mPa•s, preferably of about 100 mPa•s, and most preferably about 130 mPa•s at a relatively constant solid Mooney viscosity of 45± 5, preferably about 45. The molded core exhibits a coefficient of restitution of at least about 0.783.

In another aspect, the present invention is directed to a golf ball comprising a core formed from a core composition including a polybutadiene rubber. The polybutadiene rubber exhibits a solution viscosity of at least about

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100 mPa•s and a Mooney viscosity of from about 38 to about 52. The core exhibits a coefficient of restitution of at least about 0.785. The value of the coefficient of restitution of the core is related to the value of the solution viscosity of the polybutadiene rubber. The golf ball further includes one or more core or cover layers disposed about the core.

In yet another aspect, the present invention is directed to a method for making a molded golf ball core having a particular coefficient of restitution (C.O.R.) value, and the golf balls produced thereby. The method includes selecting a polybutadiene rubber exhibiting a particular solution viscosity value that is correlated to the particular C.O.R. value desired. The method further includes forming a composition from that polybutadiene rubber so that the composition, when molded into a solid core, has a coefficient of restitution value related to the value of the solution viscosity of the polybutadiene rubber. The method further comprises the step of covering the core so formed with one or more core or cover layers.

In yet a further aspect, the present invention is directed to a method for making a solid golf ball core. The method includes selecting a polybutadiene rubber exhibiting a particular solution viscosity value. A core composition is formed including the polybutadiene rubber. A molded, solid core is formed from the core composition, and the core exhibits a coefficient of restitution (C.O.R.) value related to the solution viscosity value of the polybutadiene rubber. If desired, one or more core and/or cover layers enclose such a core. The present invention also relates to golf balls formed by this method.

Other features and benefits of the present invention will come to light in reviewing the following written specification and accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects, features and advantages of the present invention should become apparent in the following description when taken in conjunction with the accompanying drawing, in which:

Fig. 1 shows a graph of coefficient of restitution values for each different core versus solution viscosity values for the polybutadiene rubbers that form each core.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is directed to a golf ball comprising a core produced from an improved core composition. The core composition includes a base polybutadiene rubber exhibiting enhanced solution viscosity values which, when utilized for golf ball core construction, produce cores exhibiting an enhanced C.O.R. over known core compositions. The present invention is also directed to methods for making such compositions, particularly, core compositions, having enhanced C.O.R values when utilized in golf ball construction.

The present invention is also directed to a golf ball comprising a core formed from a core composition including a polybutadiene rubber. The polybutadiene rubber exhibits a higher solution viscosity (at a relatively constant solid Mooney viscosity) over known polybutadiene rubbers used in core compositions. Preferably, the polybutadiene rubber exhibits a solution viscosity of greater than 70 mPa•s, preferably greater than about 80 mPa•s, and more preferably greater than about 90 mPa•s, at a constant solid Mooney viscosity of about 38 to about 52, more preferably 45 ± 5.

Further preferably, the polybutadiene rubber in the core composition exhibits a solution viscosity of at least about 100 mPa•s and a Mooney viscosity of from about 38 to about 52. The core formed from the core composition has a coefficient of restitution of at least about 0.783, preferably about 0.785 or more.

Most preferably, the present invention is directed to a solid, non-wound, golf ball comprising a solid, molded core formed from a core composition including polybutadiene rubber. The polybutadiene rubber exhibits a solution viscosity of about 130 mPa•s and a Mooney viscosity of from about 38 to about 52. The core that is formed from the core composition exhibits a coefficient of restitution (C.O.R.) of at least about 0.785. The value of the solution viscosity

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of the polybutadiene rubber is related to the coefficient of restitution value of the core in such a manner such that the higher the value of the solution viscosity of the polybutadiene rubber, the higher the value of the coefficient of restitution of the solid, molded core formed from such polybutadiene rubber. The Mooney viscosity of the polybutadiene rubber utilized to form the core remains relatively constant.

The solution viscosity for the polybutadiene rubbers is defined according to the standard ASTM D 445-01, herein incorporated by reference. Solution viscosity values throughout the present application are defined with the units of mPa·s. The solution viscosity can also be defined under other known international standards including DIN 51 562.

The Mooney viscosity (ML (1+4) 100 °C) value for the polybutadiene rubber is defined according to the standard ASTM D 1646-00, herein incorporated by reference. The Mooney viscosity for the polybutadiene can also be defined under other accepted international standards, including ISO 289 and DIN 53 523.

In another embodiment, the core composition can be formed from a single polybutadiene rubber or a blend of two or more polybutadiene rubbers, or a blend of polybutadiene rubber with other elastomers. When the core composition is formed from a blend of two or more polybutadiene rubbers, at least one of the polybutadiene rubbers preferably exhibits a solution viscosity of greater than 70 mPa·s, preferably 80 mPa·s and more preferably 90 mPa·s, at a relatively constant solid Mooney viscosity of about 38 to about 52, preferably 45 ± 5. The molded core has a coefficient of restitution of at least about 0.780, preferably about 0.785 or more.

The relationship between the solution viscosity and the coefficient of restitution is valuable when it is desired to achieve particular properties in a golf ball, such as a particular coefficient of restitution for the core based upon solution viscosity values for a particular polybutadiene rubber or blend of polybutadiene rubbers. Also, a higher coefficient of restitution value for the molded core can be achieved by forming the core from a core composition

including a polybutadiene rubber or blends of polybutadiene rubbers having a higher solution viscosity value.

While the solution viscosity values for the polybutadiene rubbers used in the present invention can vary, the solid Mooney viscosity of the polybutadiene rubbers remains relatively constant. As used herein, a relatively constant solid Mooney viscosity value for the polybutadiene rubber means a value within a particular range of values. Preferably, the polybutadiene rubber exhibits a Mooney viscosity of from about 38 to about 52. More preferably, the polybutadiene rubber exhibits a Mooney viscosity of from about 40 to about 50, i.e. 45 ± 5. Thus, as the preferred solid Mooney viscosity values exhibited by the polybutadiene rubbers remain relatively constant, the solution viscosity values for the polybutadiene rubbers can vary greatly. This is discussed in more detail below.

Preferably, the polybutadiene rubbers used in the present invention have a high cis-1,4 content. The preferred polybutadiene rubbers have a cis-1,4 content of at least about 96%.

The preferred polybutadiene rubbers for the core composition are the commercially available BUNA® CB series polybutadiene rubbers manufactured by the Bayer Co., Pittsburgh, PA. The BUNA® CB series polybutadiene rubbers are generally of a relatively high purity and light color. The low gel content of the BUNA® CB series polybutadiene rubbers ensures almost complete solubility in styrene. The BUNA® CB series polybutadiene rubbers have a relatively high cis-1,4 content. Preferably, each BUNA® CB series polybutadiene rubber has a cis-1,4 content of at least 96%. Additionally, each BUNA® CB series polybutadiene rubber exhibits a different solution viscosity, preferably from about 42 mPa•s to about 170 mPa•s, while maintaining a relatively constant solid Mooney viscosity value range, preferably of from about 38 to about 52. The BUNA® CB series polybutadiene rubbers preferably have a vinyl content of less than about 12%, more preferably a vinyl content of about 2%. Table 1 below discloses the commercially available BUNA® CB series polybutadiene rubbers and the solution viscosity and Mooney viscosity of each BUNA® CB series polybutadiene rubber.

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Table 1

Solution Viscosity and Mooney Viscosity of BUNA® CB Series Polybutadiene Rubbers

Property	BUNA® CB 1405	BUNA® CB 1406	BUNA® CB 1407	BUNA® CB 1409	BUNA® CB 1410
Solution Viscosity mPa•s	50 +/-7	60 +/-7	70 +/-10	90 +/-10	100 +/-10
Mooney Viscosity mL 1+4 100 °C	45 +/-5	45 +/-5	45 +/-5	45 +/-5	45 +/-5

Property	BUNA® CB 1412	BUNA® CB 1414	BUNA® CB 1415	BUNA® CB 1416	BUNA® CB 10
Solution Viscosity mPa•s	120 +/-10	140 +/-10	150 +/-10	160 +/-10	140 +/-20
Mooney Viscosity mL 1+4 100 °C	45 +/-5	45 +/-5	45 +/-5	45 +/-5	47 +/-5

Table 2 below further shows other properties exhibited by BUNA® CB 1406, BUNA® CB 1407, BUNA® CB 1409, BUNA® CB 1410, BUNA® CB 1412, BUNA® CB 1414, BUNA® CB 1415, and BUNA® CB 1416.

Table 2

Property	Test Method	Units	BUNA® CB 1406	BUNA® CB 1407	BUNA® CB 1409	BUNA® CB 1410
Catalyst			Cobalt	Cobalt	Cobalt	Cobalt
Cis-1,4 Content	IR Spectroscopy; AN-SAA 0422	%	≥96	≥96	≥96	≥96
Volatile Matter	ISO 248 /ASTM D 1416	%	≤0.5	≤0.5	≤0.5	≤0.5
Ash Content	ISO 247 /ASTM D 1416	%	≤0.1	≤0.1	≤0.1	≤0.1
Mooney Viscosity ML (1+4) 100°C	ISO 289 /DIN 53 523 /ASTM D 1646	MU	45 ±5	45 ±5	45 ±5	45 ±5

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Property	Test Method	Units				
Solution Viscosity, 5% in styrene	ASTM D 445 /DIN 51 562	mPa•s	60 ±7	70 ±7	90 ±10	100 ±10
Styrene insoluble: dry gel	08-02.08.CB	ppm	≤100	≤100	≤100	≤100
Color in styrene	ISO 6271 /ASTM D 1209	APHA	≤10	≤10	≤10	≤10
Solubility			in aliphatic hydro-carbons	in aliphatic hydro-carbons	in aliphatic hydro-carbons	in aliphatic hydro-carbons
Total Amount of Stabilizer	AN-SAA 0583	%	0.2	0.2	0.2	0.2

Property	Test Method	Units	BUNA® CB 1412	BUNA® CB 1414	BUNA® CB 1415	BUNA® CB 1416
Catalyst			Cobalt	Cobalt	Cobalt	Cobalt
Cis-1,4 Content	IR Spectroscopy; AN-SAA 0422	%	≥96	≥96	≥96	≥96
Volatile Matter	ISO 248 /ASTM D 1416	%	≤0.5	≤0.5	≤0.5	≤0.5
Ash Content	ISO 247 /ASTM D 1416	%	≤0.1	≤0.1	≤0.1	≤0.1
Mooney Viscosity ML (1+4) 100°C	ISO 289 /DIN 53 523 /ASTM D 1646	MU	45 ±5	45 ±5	45 ±5	45 ±5
Solution Viscosity, 5% in styrene	ASTM D 445 /DIN 51 562	mPa•s	120 ±10	140 ±10	150 ±10	160 ±10
Styrene insoluble: dry gel	08-02.08.CB	ppm	≤100	≤100	≤100	≤100
Color in styrene	ISO 6271 /ASTM D 1209	APHA	≤10	≤10	≤10	≤10
Solubility			in aliphatic hydro-carbons	in aliphatic hydro-carbons	in aliphatic hydro-carbons	in aliphatic hydro-carbons
Total Amount of Stabilizer	AN-SAA 0583	%	0.2	0.2	0.2	0.2

Of the above described BUNA® CB polybutadiene rubbers, the most preferred for a core composition is BUNA® CB 10 polybutadiene rubber. BUNA® CB 10 polybutadiene rubber has a relatively high cis-1,4 content, good resistance to aging, reversion, abrasion and flex cracking, good low temperature flexibility and high resilience. The BUNA® CB 10 polybutadiene rubber preferably has a vinyl content of less than about 12%, more preferably about 2% or less. Table 3 below shows the specific properties of the BUNA® CB 10 polybutadiene rubber.

Table 3
Properties of BUNA® CB 10 Polybutadiene Rubber

Raw Material Properties	Value	Unit	Test method
Volatile Matter	≤0.5	wt-%	ISO 248 /ASTM D 5668
Mooney viscosity ML(1+4) @ 100°C	47 ±5	MU	ISO 289 /ASTM D 1646
Solution viscosity, 5.43 wt % in toluene	140 ±20	mPa•s	ASTM D 445 /ISO 3105 (5% in toluene)
Cis-1,4 content	≥96	wt-%	IR Spectroscopy, AN-SAA 0422
Color, Yellowness Index	≤10		ASTM E 313-98
Cobalt content	≤5	ppm	DIN 38 406 E22
Total Stabilizer content	≥0.15	wt-%	AN-SAA 0583
Specific Gravity	0.91		
Vulcanization Properties (Test formulation from ISO 2476 / ASTM D 3189 (based on IRB 7))	**Value**	**Unit**	**Test Method**
Monsanto Rheometer MDR 2000E, 160°C/30 min./α = ±0.5°C			
Torque Minimum (ML)	3.5±0.7	dNm	ISO 6502/ASTM D5289
Torque Maximum (MH)	19.9±2.4	dNm	ISO 6502/ASTM D5289
Scorch Time, t.s. $_1$	2.9±0.6	min	ISO 6502/ASTM D5289
Cure Time, t.c. $_{50}$	8.7±1.7	min	ISO 6502/ASTM D5289
Cure Time, t.c. $_{90}$	12.8±2.4	min	ISO 6502/ASTM D5289

A core composition can include one BUNA® CB series polybutadiene rubber or a blend of two or more BUNA® CB series polybutadiene rubbers. Alternatively, the BUNA® CB series polybutadiene rubbers may be blended with one or more other polybutadiene rubbers in forming the core composition. Other preferred polybutadiene rubbers that can be blended with the BUNA® CB series polybutadiene rubbers include commercially available polybutadiene rubbers under the designation NEO CIS® 40 and NEO CIS® 60 polybutadiene rubbers, available from Enichem Elastomers America, Inc., Houston TX.

Blends of BUNA® CB series polybutadiene rubbers and other polybutadiene rubbers can include from 1 to 99 weight % of the BUNA® CB series polybutadiene rubber and from 99 to 1 weight % of a second polybutadiene rubber. The second polybutadiene rubber can be a second BUNA® CB series polybutadiene rubber or a polybutadiene rubber different from the BUNA® CB series polybutadiene rubbers. Preferably, the blend of BUNA® CB series polybutadiene rubber with a second polybutadiene rubber includes at least 50 weight % of a BUNA® CB series polybutadiene rubber and 50 weight % or less of a second polybutadiene rubber. Most preferably, the blend of polybutadiene rubbers includes at least 70 weight % of a BUNA® CB series polybutadiene rubber and 30 weight % or less of a second polybutadiene rubber.

The golf ball core is preferably formed from a cross-linked unsaturated elastomer and comprises a polybutadiene rubber. The diameter of the core is determined based upon the desired ball diameter minus the thickness of the cover layer or layers (if desired). The core generally has a diameter of about 1.0 to 1.6 inches, preferably about 1.4 to 1.6 inches.

Conventional solid cores are typically compression molded from slugs of uncured or slightly cured elastomer composition including a high cis-1,4 content polybutadiene. A small amount of a metal oxide, such as zinc oxide, may be included as a filler. Large amounts of metal oxide may be included in conventional cores in order to increase the core weight so that the finished ball more closely approaches the U.S.G.A. upper weight limit of 1.620 oz. Other materials may be used in the core composition such as compatible rubbers or

ionomers or low molecular weight fatty acids such as stearic acid. Free radical initiators such as peroxides may be added to the core composition so that on the application of heat and pressure a complex curing crosslinking reaction occurs.

The golf balls including the core composition of the present invention can be one-piece, two-piece, or multi-layer balls. Non-limiting examples of golf balls according to the present invention include a one-piece ball comprising polybutadiene rubber. Alternatively, a two-piece ball can be formed with a core formed from a core composition including polybutadiene rubber of the present invention and a cover disposed about the core. A multi-piece ball can also be formed with a core formed from a core composition including a polybutadiene rubber, a mantle or intermediate layer, and a cover disposed about the mantle. A multi-layer ball can also be formed wherein the ball includes a multi-layer core, where one or more layers of the multi-layer core is formed from a core composition including polybutadiene rubber in accordance with the present invention.

The present invention is also directed to a method for making a composition exhibiting a particular coefficient of restitution. The method includes selecting a polybutadiene rubber exhibiting a particular solution viscosity value. A composition is then formed including the polybutadiene rubber. The composition formed exhibits a coefficient of restitution value related to the solution viscosity value of the polybutadiene rubber. Preferably, as the solution viscosity of the selected polybutadiene rubber is higher, the value of the coefficient of restitution for the molded core formed from the polybutadiene rubber is higher. The Mooney viscosity of the polybutadiene rubber exhibits a relatively constant value, preferably from about 38 to about 52, more preferably 45 ± 5.

The present invention also relates to a method for making a golf ball core exhibiting a particular coefficient of restitution. The method includes selecting a polybutadiene rubber exhibiting a particular solution viscosity value. A core composition is formed including the polybutadiene rubber. A core is then formed from the core composition. The core exhibits a coefficient of restitution that is related to the solution viscosity of the polybutadiene rubber. As the

solution viscosity value of the polybutadiene rubber can vary, the Mooney viscosity exhibited by the polybutadiene rubber remains relatively constant, preferably from about 38 to about 52, as indicated above.

The free radical initiator included in the core composition is any known polymerization initiator (a co-crosslinking agent) which decomposes during the cure cycle. The term "free radical initiator" as used herein refers to a chemical which, when added to a mixture of the elastomeric blend and a metal salt of an unsaturated, carboxylic acid, promotes crosslinking of the elastomers by the metal salt of the unsaturated carboxylic acid. The amount of the selected initiator present is dictated only by the requirements of catalytic activity as a polymerization initiator. Suitable initiators include peroxides, persulfates, azo compounds and hydrazides. Peroxides which are readily commercially available are conveniently used in the present invention, generally in amounts of from about 0.1 to about 10.0 and preferably in amounts of from about 0.3 to about 3.0 parts by weight per each 100 parts of elastomer, wherein the peroxide has a 40% level of active peroxide.

Exemplary of suitable peroxides for the purposes of the present invention are dicumyl peroxide, n-butyl 4,4'-bis (butylperoxy) valerate, 1,1-bis(t-butylperoxy)-3,3,5-trimethyl cyclohexane, di-t-butyl peroxide and 2,5-di-(t-butylperoxy)-2,5 dimethyl hexane and the like, as well as mixtures thereof. It will be understood that the total amount of initiators used will vary depending on the specific end product desired and the particular initiators employed. Examples of such commercially available peroxides are known in the art.

Preferred co-agents which can be used with the above peroxide polymerization agents include zinc diacrylate, zinc dimethacrylate, trimethloyl propane triacrylate, and trimethloyl propane trimethacrylate, most preferably zinc diacrylate. Other co-agents may also be employed and are known in the art. All of these co-agents are commercially available.

The unsaturated carboxylic acid component of the core composition (a co-crosslinking agent) is the reaction product of the selected carboxylic acid or acids and an oxide or carbonate of a metal such as zinc, magnesium, barium, calcium, lithium, sodium, potassium, cadmium, lead, tin,

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and the like. Preferably, the oxides of polyvalent metals such as zinc, magnesium and calcium are used, and most preferably, the oxide is zinc oxide.

Exemplary of the unsaturated carboxylic acids which find utility in the present core compositions are acrylic acid, methacrylic acid, itaconic acid, crotonic acid, sorbic acid, and the like, and mixtures thereof. Preferably, the acid component is either acrylic or methacrylic acid. Usually, from about 15 to about 25, and preferably from about 17 to about 21 parts by weight of the carboxylic acid salt, such as zinc diacrylate, is included in the core composition. The unsaturated carboxylic acids and metal salts thereof are generally soluble in the elastomeric base, or are readily dispersible.

Unsaturated polycarboxylic acids which may be employed in the compositions of the invention include maleic acid, fumaric acid, itaconic acid and the like, preferably fumaric acid. Use of fumaric acid in compositions including polybutadiene and epoxy resins is shown in U.S. Pat. No. 3,671,477.

In addition to the foregoing, filler materials can be employed in the compositions of the invention to control the weight of the ball. Fillers which are incorporated into the compositions should be in finely divided form, typically in a size generally less than about 20 mesh, preferably less than about 100 mesh U.S. standard size. Preferably, the filler is one with a high specific gravity, such as zinc oxide. Other fillers which may be employed include, for example, silica, clay, talc, mica, asbestos, glass, glass fibers, barytes (barium sulfate), limestone, lithophone (zinc sulphide-barium sulfate), titanium dioxide, zinc sulphide, calcium metasilicate, silicon carbide, diatomaceous earth, particulate carbonaceous materials, micro balloons, aramid fibers, particulate synthetic plastics such as high molecular weight polyethylene, polystyrene, polyethylene, polypropylene, ionomer resins and the like, as well as cotton flock, cellulose flock and leather fiber. Powdered metals such as titanium, tungsten, aluminum, bismuth, nickel, molybdenum, copper, brass and their alloys also may be used as fillers. The amount of filler employed is primarily a function of weight restrictions on the weight of a golf ball made from those compositions.

The compositions of the invention also may include various processing aids known in the rubber and molding arts, such as fatty acids.

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Generally, free fatty acids having from about 10 carbon atoms to about 40 carbon atoms, preferably having from about 15 carbon atoms to about 20 carbon atoms, may be used. Fatty acids which may be used include stearic acid and linoleic acids, as well as mixtures thereof. When included in the compositions of the invention, the fatty acid component is present in amounts of from about 1 part by weight per 100 parts elastomer, preferably in amounts of from about 2 parts by weight per 100 parts elastomer to about 5 parts by weight per 100 parts elastomer. Examples of processing aids which may be employed include, for example, calcium stearate, barium stearate, zinc stearate, lead stearate, basic lead stearate, dibasic lead phosphite, dibutyltin dilaurate, dibutyltin dimealeate, dibutyltin mercaptide, as well as dioctyltin and stannane diol derivatives.

Coloring pigments also may be included in the compositions of the invention. Useful coloring pigments include, for example, titanium dioxide, the presence of which simplifies the surface painting operation of a one piece golf ball. In some cases, coloring pigments eliminate the need for painting such as, for example, a one piece golf ball intended for use on driving ranges.

The core compositions of the present invention may additionally contain any other suitable and compatible modifying ingredients including, but not limited to, metal oxides, fatty acids, and diisocyanates and polypropylene powder resin.

Various activators may also be included in the compositions of the present invention. For example, zinc oxide and/or magnesium oxide are activators for the polybutadiene. The activator can range from about 2 to about 50 parts by weight per 100 parts by weight of the rubbers (phr) component, preferably at least 3 to 5 parts by weight per 100 parts by weight of the rubbers.

Higher specific gravity fillers may be added to the core composition so long as the specific core weight limitations are met. The amount of additional filler included in the core composition is primarily dictated by weight restrictions and preferably is included in amounts of from about 0 to about 100 parts by weight per 100 parts rubber. Ground flash filler may be incorporated and is preferably mesh ground up center stock from the excess flash from

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compression molding. It lowers the cost and may increase the hardness of the ball.

Diisocyanates may also be optionally included in the core compositions. When utilized, the diisocyanates are included in amounts of from about 0.2 to about 5.0 parts by weight based on 100 parts rubber. Exemplary of suitable diisocyanates is 4,4'-diphenylmethane diisocyanate and other polyfunctional isocyanates known to the art.

Furthermore, the dialkyl tin difatty acids set forth in U.S. Pat. No. 4,844,471, the dispersing agents disclosed in U.S. Pat. No. 4,838,556, and the dithiocarbamates set forth in U.S. Pat. No. 4,852,884 may also be incorporated into the polybutadiene compositions of the present invention. The specific types and amounts of such additives are set forth in the above identified patents, which are incorporated herein by reference.

A golf ball formed from compositions of the invention may be made by conventional mixing and compounding procedures used in the rubber industry. For example, the ingredients may be intimately mixed using, for example, two roll mills or a BANBURY® mixer, until the composition is uniform, usually over a period of from about 5 to 20 minutes. The sequence of addition of components is not critical. A preferred blending sequences is as follows.

The elastomer, fillers, zinc salt, metal oxide, fatty acid, and the metallic dithiocarbamate (if desired), surfactant (if desired), and tin difatty acid (if desired), are blended for about 7 minutes in an internal mixer such as a BANBURY® mixer. As a result of shear during mixing, the temperature rises to about 200°F. The initiator and diisocyanate are then added and the mixing continued until the temperature reaches about 220°F whereupon the batch is discharged onto a two roll mill, mixed for about one minute and sheeted out. The mixing is desirably conducted in such a manner that the composition does not reach incipient polymerization temperature during the blending of the various components.

The composition can be formed into a core structure by any one of a variety of molding techniques, e.g. injection, compression, or transfer molding. If the core is compression molded, the sheet is then rolled into a "pig"

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and then placed in a BARWELL® preformer and slugs are produced. The slugs are then subjected to compression molding at about 320°F for about 14 minutes. After molding, the molded cores are cooled at room temperature for about 4 hours or in cold water for about one hour.

Usually the curable component of the composition will be cured by heating the composition at elevated temperatures on the order of from about 275°F to about 350°F, preferably and usually from about 290°F to about 325°F, with molding of the composition effected simultaneously with the curing thereof. When the composition is cured by heating, the time required for heating will normally be short, generally from about 10 to about 20 minutes, depending upon the particular curing agent used. Those of ordinary skill in the art relating to free radical curing agents for polymers are conversant with adjustments to cure times and temperatures required to effect optimum results with any specific free radical agent.

After molding, the core is removed from the mold and the surface may be treated to facilitate adhesion thereof to the covering materials. Surface treatment can be effected by any of the several techniques known in the art, such as corona discharge, ozone treatment, sand blasting, and the like. Preferably, surface treatment is effected by grinding with an abrasive wheel (centerless grinding) whereby a thin layer of the molded core is removed to produce a round core having a diameter of 1.28 to 1.63 inches, preferably about 1.37 to about 1.54 inches, and most preferably, 1.42 inches. Alternatively, the cores are used in the as-molded state with no surface treatment.

One or more cover layers can be applied about the present core in accordance with procedures known in the art. Any known cover composition to form a cover can be used. U.S. Patent Nos. 6,277,921; 6,220,972; 6,150,470; 6,126,559; 6,117,025; 6,100,336; 5,779,562; 5,688,869; 5,591,803; 5,542,677; and 5,368,304, herein entirely incorporated by reference, disclose cover compositions, layers, and properties suitable for forming golf balls in accordance with the present invention.

When utilized herein, various properties of the balls are determined as follows:

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Coefficient of Restitution

The coefficient of restitution is the ratio of the outgoing velocity to the incoming velocity. In the examples of this application, the coefficient of restitution was measured by propelling a ball or core horizontally at a speed of 125 +/- 5 feet per second (fps) against a generally vertical, hard, flat steel plate and measuring the ball's incoming and outgoing velocities electronically. Speeds were measured with a pair of Oehler Mark 55 ballistic screens available from Oehler Research, Inc., Austin, TX, which provide a timing pulse when an object passes through them. The screens were separated by 36 inches and were located 25.25 inches and 61.25 inches from the rebound wall. The ball speed was measured by timing the pulses from screen 1 to screen 2 on the way into the rebound wall (as the average speed of the ball over 36 inches), and then the exit speed was timed from screen 2 to screen 1 over the same distance. The rebound wall was tilted 2 degrees from a vertical plane to allow the ball to rebound slightly downward in order to miss the edge of the cannon that fired it. The rebound wall was solid steel 2.0 inches thick.

The incoming speed should be 125±5 fps but corrected to 125 fps. The correlation between C.O.R. and forward or incoming speed has been studied and a correction has been made over the ±5 fps range so that the C.O.R. is reported as if the ball had an incoming speed of exactly 125.0 fps.

Compression

PGA compression is another important property involved in the performance of a golf ball. The compression of the ball can affect the playability of the ball on striking and the sound or "click" produced. Similarly, compression can effect the "feel" of the ball (i.e., hard or soft responsive feel), particularly in chipping and putting.

Moreover, while compression itself has little bearing on the distance performance of a ball, compression can affect the playability of the ball on striking. The degree of compression of a ball against the club face and the softness of the cover, if applicable, strongly influence the resultant spin rate. Typically, a softer cover will produce a higher spin rate than a harder cover.

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Additionally, a harder core will produce a higher spin rate than a softer core. This is because at impact a hard core serves to compress the cover of the ball against the face of the club to a much greater degree than a soft core thereby resulting in more "grab" of the ball on the clubface and subsequent higher spin rates. In effect the cover is squeezed between the relatively incompressible core and clubhead. When a softer core is used, the cover is under much less compressive stress than when a harder core is used and therefore does not contact the clubface as intimately. This results in lower spin rates.

The term "compression" utilized in the golf ball trade generally defines the overall deflection that a golf ball undergoes when subjected to a compressive load. For example, PGA compression indicates the amount of change in a golf ball's shape upon striking. The development of solid core technology in two-piece balls has allowed for much more precise control of compression in comparison to thread wound three-piece balls. This is because in the manufacture of solid core balls, the amount of deflection or deformation is precisely controlled by the chemical formula used in making the cores. This differs from wound three-piece balls wherein compression is controlled in part by the winding process of the elastic thread. Thus, two-piece and multilayer solid core balls exhibit much more consistent compression readings than balls having wound cores.

PGA compression relates to a scale of from 0 to 200 given to a golf ball. The lower the PGA compression value, the softer the feel of the ball upon striking. In practice, tournament quality balls have compression ratings around 70 to 110, and preferably around 80 to 100.

In determining PGA compression using the 0 to 200 scale, a standard force is applied to the external surface of the ball. A ball which exhibits no deflection (0.0 inches in deflection) is rated 200 and a ball which deflects 2/10th of an inch (0.2 inches) is rated 0. Every change of .001 of an inch in deflection represents a 1 point drop in compression. Consequently, a ball which deflects 0.1 inches (100 x .001 inches) has a PGA compression value of 100 (i.e., 200 to 100) and a ball which deflects 0.110 inches (110 x .001 inches) has a PGA compression of 90 (i.e., 200 to 110).

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An example to determine PGA compression can be shown by utilizing a golf ball compression tester produced by OK Automation, Sinking Spring PA (formerly Atti Engineering Corporation). The value obtained by this tester relates to an arbitrary value expressed by a number which may range from 0 to 100, although a value of 200 can be measured as indicated by two revolutions of the dial indicator on the apparatus. The value obtained defines the deflection that a golf ball undergoes when subjected to compressive loading. The compression test apparatus consists of a lower movable platform and an upper movable spring-loaded anvil. The dial indicator is mounted such that it measures the upward movement of the springloaded anvil. The golf ball to be tested is placed in the lower platform, which is then raised a fixed distance. The upper portion of the golf ball comes in contact with and exerts a pressure on the springloaded anvil. Depending upon the distance of the golf ball to be compressed, the upper anvil is forced upward against the spring.

Alternative devices have also been employed to determine compression. For example, Applicant also utilizes a modified Riehle Compression Machine originally produced by Riehle Bros. Testing Machine Company, Philadelphia, PA to evaluate compression of the various components (i.e., cores, mantle cover balls, finished balls, etc.) of the golf balls. The Riehle compression device determines deformation in thousandths of an inch under a load designed to emulate the 200 pound spring constant of the other compression testers. Using such a device, a Riehle compression of 61 corresponds to a deflection under load of 0.061 inches. Other examples of compression devices include a Whitney Tester or an Instron™. A set relationship or formula is used to correlate or correspond to PGA compression.

Additionally, an approximate relationship between Riehle compression and PGA compression exists for balls of the same size. It has been determined by Applicant that Riehle compression corresponds to PGA compression by the general formula PGA compression = 160 - Riehle compression. Consequently, 80 Riehle compression corresponds to 80 PGA compression, 70 Riehle compression corresponds to 90 PGA compression, and 60 Riehle compression corresponds to 100 PGA compression. For reporting

purposes, Applicant's compression values are usually measured as Riehle compression and converted to PGA compression.

The present invention is further illustrated by the following example in which the parts of the specific ingredients are by weight. It is to be understood that the present invention is not limited to the example, and various changes and modifications may be made in the invention without departing from the spirit and scope thereof.

Example

Core compositions 1-12 were formed from the formulations shown in Table 4 below. Core compositions 1 and 2 are comparative core compositions, where core composition 1 is formed from CARIFLEX® BR 1220 polybutadiene rubber and core composition 2 is formed from TAKTENE® 220 polybutadiene rubber.

Table 4

	1	2	3	4	5	6	7	8	9	10	11	12
CARIFLEX® BR 1220	100											
TAKTENE® 220		100										
BUNA® CB 1405			100									
BUNA® CB 1406				100								
BUNA® CB 1407					100							
BUNA® CB 1409						100						
BUNA® CB 1410							100					
BUNA® CB 1412								100				
BUNA® CB 1414									100			
BUNA® CB 1415										100		
BUNA® CB 1416											100	
BUNA® CB 10												100
ZnO	22.3	22.3	22.3	22.3	22.3	22.3	22.3	22.3	22.3	22.3	22.3	22.3
T.G. Regrind	20	20	20	20	20	20	20	20	20	20	20	20
Zn Stearate	20	20	20	20	20	20	20	20	20	20	20	20
ZDA	24	24	24	24	24	24	24	24	24	24	24	24
Peroxide	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90

Each of the core compositions 1-12 were molded into golf ball cores and were tested for the particular properties. Table 5 below shows the test results.

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Table 5

Sample No.	1	2	3	4	5	6
Size (inches)	1.542	1.542	1.541	1.543	1.543	1.543
Weight (grams)	36.4	36.3	36.3	36.4	36.4	36.5
Compression (Riehle)	88	94	91	90	89	88
C.O.R.	.783	.774	.777	.777	.781	.783
Nes Factor[1]	871	868	868	867	870	871
Solution Viscosity mPa·s	65-70	60	50	60	70	90
MDR s'max torque	81.9	72.2	76.1	77.5	82.1	82.9
Mooney Viscosity ±5	40	41	45	45	45	45

Sample No.	7	8	9	10	11	12
Size (inches)	1.543	1.543	1.546	1.543	1.543	1.544
Weight (grams)	36.5	36.4	36.5	36.4	36.4	36.5
Compression (Riehle)	87	88	86	87	85	89
C.O.R.	.785	.784	.788	.787	.788	.786
Nes Factor[1]	873	872	874	874	873	875
Solution Viscosity mPa·s	100	120	140	150	160	140
MDR s'max torque	82.4	81.3	79.9	80.3	80.7	77.4
Mooney Viscosity ±5	45	45	45	45	45	45

[1]The Nes Factor is the sum of the Riehle Compression and the C.O.R. (x1000). The higher the Nes Factor number, the higher the resilience.

The values of the solution viscosity and coefficient of restitution for each core composition were compared in a graph shown in FIGURE 1. Based on the graph shown in FIGURE 1, a relationship exists between the solution viscosity for each polybutadiene rubber and the coefficient of restitution for each core. Particularly, FIGURE 1 shows that the greater the value of the solution viscosity for a polybutadiene rubber, the greater the value of the coefficient of restitution for the molded core including the polybutadiene rubber. While a relationship exists between the solution viscosity value of the

polybutadiene rubber and the coefficient of restitution value of the core, the Mooney viscosity for the polybutadiene rubber remained at a relatively constant value.

It is also shown in FIGURE 1 and Table 5 that the controls (core composition 1, which includes CARIFLEX® BR 1220 polybutadiene rubber, and core composition 2, which includes TAKTENE® 220 polybutadiene rubber), have a lower solution viscosity and coefficient of restitution when compared to core compositions 6-12. Core compositions 6-12 each have a solution viscosity of at least about 90 mPa•s and a coefficient of restitution of at least about 0.783. Therefore, based upon the measurement of properties of core compositions 1-12, the greater the value of the solution viscosity of the polybutadiene rubber, the greater the value of the coefficient of restitution of the core composition including the higher solution viscosity polybutadiene rubber.

Although the preferred embodiments of the present invention have been described in detail, various modifications, alterations and changes or equivalents thereof may be made without departing from the spirit and scope of the invention.